

(19)



Europäisch Patentamt
Europ an Pat nt Office
Office uropé n des br vets



(11) Publication number : **0 571 091 A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number : **93303329.2**

(22) Date of filing : **28.04.93**

(51) Int. Cl.⁵ : **C10M 105/38, C10M 105/42,
C10M 169/04, C10M 171/00,
// (C10M169/04, 105:38,
105:42, 133:44, 137:02,
137:12), C10N40:30**

(30) Priority : **29.04.92 US 874946**

(43) Date of publication of application :
24.11.93 Bulletin 93/47

(84) Designated Contracting States :
**AT BE CH DE DK ES FR GB GR IE IT LI LU MC
NL PT SE**

(71) Applicant : **The Lubrizol Corporation
29400 Lakeland Boulevard
Wickliffe, Ohio 44092 (US)**

(72) Inventor : **Jolley, Scott Ted
7094 Victoria Drive
Mentor, Ohio 44060 (US)
Inventor : Davis, Kirk Emerson
12912 S. Woodside Drive
Chester Township, Ohio 44026 (US)**

(74) Representative : **Mallalieu, Catherine Louise et
al
D. Young & Co., 21 New Fetter Lane
London EC4A 1DA (GB)**

(54) **Liquid compositions containing carboxylic esters.**

(57) This invention relates to a liquid composition comprising (A) at least one fluorine-containing hydrocarbon containing one to three carbon atoms, and a lubricant comprising (B) at least one ester lubricant selected from the group consisting of (i) an ester of a polyhydroxy compound and a monocarboxylic acylating agent having from about 4 to about 15 carbon atoms, and (ii) an ester of polyhydroxy compound and a combination of a dicarboxylic acylating agent and a monocarboxylic acylating agent having about 7 to about 15 carbon atoms, and (C) at least one additive selected from the group consisting of an alkyl phosphite, an alkyl phosphonic acid ester, a nitrogen-containing heterocycle, and a mixture thereof. Liquid compositions also are described wherein the fluorine-containing hydrocarbons also contain other halogens such as chlorine. Methods of lubricating refrigeration systems are also described. The liquid compositions are useful particularly as refrigeration liquids in refrigerators and air-conditioners including automotive, home, commercial and industrial air-conditioners.

EP 0 571 091 A1

Field of the Invention

This invention relates to liquid compositions comprising at least one fluorine-containing hydrocarbon, and at least one lubricant. More particularly, the invention relates to liquid compositions useful as refrigeration liquids.

Background of the Invention

Chlorofluorocarbons, generally referred to in the industry as CFCs, have been widely used as propellants in aerosols, although use in aerosols has been diminishing in recent years because of demands of environmentalists for the reduction if not a complete ban on the use of CFCs because of the detrimental effect of CFCs on the stratosphere's ozone layer. CFCs also have been used because of their unique combination of properties as refrigerants, foam-blowing agents, and specialty solvents within the electronics and aerospace industries. Examples of CFCs which have been utilized for these purposes include CFC-13 which is chlorotrifluoromethane, CFC-12 which is dichlorodifluoromethane, and CFC-113 which is 1,2,2-trifluoro-1,1,2-trichloroethane.

Since 1976, when the aerosol industry began to feel the pressure to reduce if not eliminate the use of CFCs, the aerosol industry has progressively moved toward the substitution of hydrocarbon propellants for CFC propellants. The hydrocarbons, such as butane, are readily available and inexpensive, and the quality of the final product generally has been unaffected by the substitution of propellants. However, the problem of finding a safe replacement of CFC refrigerants and foam-blowing agents has been more difficult to solve. Several replacement candidates have been suggested as alternatives to the fully halogenated hydrocarbons, and these include halogenated hydrocarbons containing at least some hydrogen atoms such as HCFC-22 which is difluorochloromethane, HCFC-123 which is 1,1-dichloro-2,2,2-trifluoroethane, HFC-134a which is 1,1,1,2-tetrafluoroethane and HCFC-141b which is 1,1-dichloro-1-fluoroethane.

The ozone depletion potential of these proposed substitutes is significantly less than the ozone depletion potential of the previously used CFCs. The ozone depletion potential is a relative measure of the capability of the material to destroy the ozone layer in the atmosphere. It is a combination of the percentage by weight of chlorine (the atom that attacks the ozone molecule) and the lifetime in the atmosphere. HCFC-22 and HFC-134a generally are recommended as being candidates in refrigerant applications, and HFC-134a is particularly attractive because its ozone depletion potential has been reported as being zero.

In order for any of the replacement materials to be useful as refrigerants, the materials must be compatible with the lubricant utilized in the compressor. The presently used refrigerants such as CFC-12 are readily compatible with mineral lubricating oils which are utilized as the lubricant in air-conditioner compressors. The above-described refrigerant candidates, however, have different solubility characteristics than the refrigerants presently in use. For example, mineral lubricating oil is incompatible (i.e., insoluble) with HFC-134a. Such incompatibility results in unacceptable compressor life in compression-type refrigeration equipment including refrigerators and air-conditioners including auto, home, commercial, and industrial air-conditioners.

In order to perform as a satisfactory refrigeration liquid, the mixture of refrigerant and lubricant must be compatible and stable over a wide temperature range such as from about 0°C and above 80°C or above. For some uses, it is generally desirable for the lubricants to be soluble in the refrigerant at concentrations corresponding to the ratios customary in the environment of use, e.g. about 5 to 15%, over a temperature range from -30°, or preferably -40°C, or below, to 80°C or above. In addition to thermal stability, the refrigeration liquids must have acceptable viscosity characteristics which are retained even at high temperatures, and the refrigeration liquid should not have a detrimental effect on materials used as seals in the compressors.

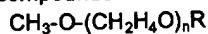
Compositions comprising a tetrafluoroethane and polyoxyalkylene glycols are discussed in U.S. Patent 4,755,316. The compositions are useful in refrigeration systems. Refrigeration oils are described in U.S. Patents 4,248,726 and 4,267,064 which comprise mixtures of a polyglycol and 0.1 to 10% of glycidyl ether type epoxy compounds, or epoxidized fatty acid monoesters, and optionally, epoxidized vegetable oil. The lubricating oils are reported to be useful in refrigerators using a halogen-containing refrigerant such as Freons 11, 12, 13, 22, 113, 114, 500 and 502 (available from DuPont), and in particular with Freon 12 or 22.

U.S. Patent 4,431,557 describes fluid compositions comprised of a fluoro- and chloro-containing refrigerant, a hydrocarbon oil, and an alkyl ne oxide additive compound which improves the thermal resistance of the oil in the presence of the refrigerant. Examples of hydrocarbon oils include mineral oil, alkyl benzene oil, dibasic acid ester oil, polyglycols, etc. The composition may contain other additives including load-carrying additives such as phosphorus acid esters, phosphoric acid esters, etc. Examples of fluorocarbon refrigerants include R-11, R-12, R-113, R-114, R-500, etc.

U.S. Patent 4,428,854 describes absorption refrigerant compositions for use in refrigeration systems com-

prising 1,1,1,2-tetrafluoroethane and an organic solvent capable of dissolving the ethane. Among the solvents disclosed are organic amides, acetonitrile, N-methyl pyrroles, N-methyl pyrrolidine, N-methyl-2-pyrrolidone, nitromethane, various dioxane derivatives, glycol ethers, butyl formate, butyl acetate, diethyl oxalate, diethyl malonate, acetone, methyl ethyl ketone, other ketones and aldehydes, triethyl phosphoric triamide, triethylene phosphate, triethyl phosphate, etc.

Stabilized absorption compositions comprising (a) a halogenated hydrocarbon refrigerant, (b) a liquid absorbent of a polyethylene glycol methyl ether, and (c) at least one stabilizer are described in U.S. Patent 4,454,052. Examples of stabilizers include phosphate esters, epoxy compounds, and organotin compounds. The polyethylene glycol methyl ether-type compounds are of the general formula



wherein n is an integer of 1 to 6, and R is H, CH_3 - or $\text{CH}_3\text{CO-}$. A variety of halogenated hydrocarbons are described including 1,1-difluoromethane, 1,1,1,2-tetrafluoroethane, etc.

U.S. Patent 4,559,154 relates to absorption heat pumps utilizing as working fluid, a saturated fluorohydrocarbon or fluorohydrocarbon ether having from 3 to 5 carbon atoms. Solvents reported to be useful with such fluorohydrocarbons include ethers such as tetraglyme, amides which can be lactams such as the N-alkyl pyrrolidones, sulfonamides and ureas including cyclic ureas.

Summary of the Invention

According to one aspect of the present invention there is provided a liquid composition comprising (A) at least one fluorine-containing hydrocarbon containing one to three carbon atoms, and a lubricant comprising (B) at least one ester lubricant selected from the group consisting of (i) an ester of a polyhydroxy compound and a monocarboxylic acylating agent having from about 4 to about 15 carbon atoms, and (ii) an ester of polyhydroxy compound and a combination of a dicarboxylic acylating agent and a monocarboxylic acylating agent having about 7 to about 15 carbon atoms, and (C) at least one additive selected from the group consisting of an alkyl phosphite, an alkyl phosphonic acid ester, a nitrogen-containing heterocycle, and a mixture thereof.

In another aspect, the invention relates to a liquid composition comprising (A) a major amount of at least one fluorine-containing hydrocarbon containing 1 or 2 carbon atoms; (B) a minor amount of at least one soluble organic lubricant comprising at least one carboxylic ester of a polyhydroxy compound containing at least 2 hydroxy groups and characterized by the general formula



wherein R is a hydrocarbyl group, each R^1 is independently hydrogen, a straight chain lower hydrocarbyl group, a branched chain hydrocarbyl group, or a straight chain hydrocarbyl group containing from 8 to about 22 carbon atoms provided that at least one R^1 group is hydrogen, a lower straight chain hydrocarbyl or a branched chain hydrocarbyl group, or a carboxylic acid- or carboxylic acid ester-containing hydrocarbyl group, and n is at least 2; and (C) a phosphite.

In another aspect, the invention relates to a liquid composition comprising (A) at least one fluorine-containing hydrocarbon containing 1 to 2 carbon atoms, and a lubricant (B) at least one ester lubricant selected from the group consisting of (i) an ester of a polyhydroxy compound and a monocarboxylic acylating agent selected from the group consisting of branched monocarboxylic acylating agents having from about 4 to about 20 carbon atoms, straight chain monocarboxylic acylating agents having from 8 to about 22 carbon atoms, and mixtures thereof, and (ii) an ester of polyhydroxy compound and a combination of a dicarboxylic acylating agent and a monocarboxylic acylating agent selected from the group consisting of branched monocarboxylic acylating agents having from about 4 to about 20 carbon atoms, straight chain monocarboxylic acylating agents having from 8 to about 22 carbon atoms, and mixtures thereof, and (C) at least one additive selected from the group consisting of an alkyl phosphite, an alkyl phosphonic acid ester, a nitrogen-containing heterocycle, and a mixture thereof.

Liquid compositions also are described wherein the fluorine-containing hydrocarbons also contain other halogens such as chlorine. Methods of lubricating refrigeration systems are also described. The liquid compositions are useful particularly as refrigeration liquids in refrigerators and air-conditioners including automotive, home, commercial and industrial air-conditioners.

Various preferred features and embodiments of the present invention will now be described by way of non-limiting example.

Throughout this specification and claims, all parts and percentages are by weight, temperatures are in degrees Celsius, and pressures are at or near atmospheric pressure unless otherwise clearly indicated.

As used in this specification and in the appended claims, the terms "hydrocarbyl" and "hydrocarbylene" denote a group having a carbon atom directly attached to the polar group and having a hydrocarbon or predominantly hydrocarbon character within the context of this invention. Such groups include the following:

(1) Hydrocarbon groups; that is, aliphatic, (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl or cycloalkenyl), and the like, as well as cyclic groups wherein the ring is completed through another portion of the molecule (that is, any two indicated substituents may together form an alicyclic group). Such groups are known to those skilled in the art. Examples include methyl, ethyl, octyl, decyl, octadecyl, cyclohexyl, etc.

(2) Substituted hydrocarbon groups; that is, groups containing non-hydrocarbon substituents which, in the context of this invention, do not alter the predominantly hydrocarbon character of the group. Those skilled in the art will be aware of suitable substituents. Examples include halo, hydroxy, alkoxy, etc.

(3) Hetero groups; that is, groups which, while predominantly hydrocarbon in character within the context of this invention, contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms will be apparent to those skilled in the art and include, for example, nitrogen, oxygen and sulfur.

In general, no more than about three substituents or hetero atoms, and preferably no more than one, will be present for each 10 carbon atoms in the hydrocarbyl group.

Terms such as "alkyl", "alkylene", etc. have meanings analogous to the above with respect to hydrocarbyl and hydrocarbylene.

The term "hydrocarbon-based" also has the same meaning and can be used interchangeably with the term hydrocarbyl when referring to molecular groups having a carbon atom attached directly to the polar group.

The term "lower" as used herein in conjunction with terms such as hydrocarbyl, hydrocarbylene, alkylene, alkyl, alkenyl, alkoxy, and the like, is intended to describe such groups which contain a total of up to 7 carbon atoms, per se, and includes methyl, ethyl, propyl, butyl, pentyl, hexyl, and heptyl groups.

Viscosity, unless otherwise indicated, is kinematic viscosity and is measured by ASTM D-2270.

For purpose of this invention, equivalent weight of polyol is determined by dividing the formula weight of the polyol by the number of hydroxyl groups. Equivalents of polyol is determined by dividing the amount of polyol by its equivalent weight. For polycarboxylic acylating agents or anhydrides, the equivalent weight is determined by dividing the formula weight of the acylating agent or anhydride by the number of carboxylic groups which form esters. For example, an anhydride contributes two carboxyl groups which can form ester. Therefore, the equivalent weight of anhydride, such as succinic anhydride, would be the formula weight of the anhydride divided by the number of carboxyl group. For succinic anhydride, the number is two.

When a compound or component is indicated herein as being "soluble", the compound or component is soluble in the liquid compositions of the invention comprising the fluorine-containing hydrocarbon and the lubricant. For example, a compound or component is considered "soluble" so long as it is soluble in the liquid compositions, even though it may be insoluble in the fluorine-containing hydrocarbon per se.

The term "consisting essentially of" refers to compositions that include the ingredients listed in the claim as well as other ingredients that do not materially affect the basic and novel characteristics of the liquid compositions.

Generally the amount of fluorine-containing hydrocarbon is a major amount for automotive and commercial and industrial refrigeration systems. Of course, lower amounts, e.g. less than 50%, of the fluorine-containing hydrocarbon are useful, such as in household refrigerators.

(A) Fluorine-Containing Hydrocarbon.

The liquid compositions include at least one fluorine-containing hydrocarbon. That is, the fluorine-containing hydrocarbons contain at least one C-H bond, as well as C-F bonds. In addition to these two essential types of bonds, the hydrocarbon also may contain other carbon-halogen bonds such as C-Cl bonds. Because the liquid compositions of the present invention are primarily intended for use as refrigerants, the fluorine-containing hydrocarbon preferably contains one to three, or to two carbon atoms, and more preferably two carbon atoms.

As noted above, the fluorine-containing hydrocarbons useful in the liquid compositions of the present invention may contain other halogens such as chlorine. However, in one preferred embodiment, the hydrocarbon contains only carbon, hydrogen and fluorine. These compounds containing only carbon, hydrogen and fluorine are referred to herein as fluorohydrocarbons or hydrofluorocarbons. The hydrocarbons containing chlorine as well as fluorine and hydrogen are referred to as chlorofluorohydrocarbons or hydrochlorofluorocarbons. The fluorine-containing hydrocarbons useful in the composition of the present invention are to be distinguished from the fully halogenated hydrocarbons which have been and are being used as propellants, refrigerants and blowing agents such as CFC-11, CFC-12 and CFC-113 which have been described above.

Specific examples of the fluorine-containing hydrocarbons useful in the liquid compositions of the present invention, and their reported ozone depletion potentials are shown in the following Table I.

TABLE I

Compound Designation	Formula	ODP*
HCFC-22	CHClF_2	0.05
HCFC-123	CHCl_2CF_3	< 0.05
HCFC-141b	$\text{CH}_3\text{CCl}_2\text{F}$	< 0.05
HFC-134a	CH_2FCF_3	0

* Ozone depletion potential as reported in Process Engineering, pp. 33-34, July, 1988.

Examples of other fluorine-containing hydrocarbons which may be useful in the liquid compositions of the present invention include trifluoromethane (HFC-23), 1,1,1-trifluoroethane (HFC-143a), 1,1-difluoroethane (HFC-152a), 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124), 1-chloro-1,1,2,2-tetrafluoroethane (HCFC-124a), 1-chloro-1,1-difluoroethane (HCFC-142b), and 1,1,2,2-tetrafluoroethane (HFC-134). Other refrigerants such as perfluoropropane (HFC-218), perfluorocyclopropane (HFC-216), perfluoropropylene oxide, 1,3-perfluoro propylene oxide and pentafluorodimethyl ether may be used with the lubricant. In the refrigerant art, the fluorohydrocarbons are often identified merely with the prefix "R" in place of the above letters. For example HFC-23 is R-23, and HCFC-124 is R-124, etc.

In general, fluorine-containing hydrocarbons which are useful as refrigerants are fluoromethanes and fluoroethanes boiling at a relatively low temperature at atmospheric pressure, e.g., below 30°C. Mixtures of fluorine-containing hydrocarbons may be used, and the amount of each fluorohydrocarbon in the mixture may be varied as desired. Examples of fluorohydrocarbon mixtures useful as (A) include: 142(b)/22; 134(a)/23; 22/124/152(a), etc. The useful fluorocarbon refrigerants serve to transfer heat in a refrigeration system by evaporating and absorbing heat at a low temperature and pressure, e.g., near ambient temperature and atmospheric pressure, and by releasing heat on condensing at a higher temperature and pressure.

The amount of fluorine-containing hydrocarbon is the level typically used for the refrigeration system. The liquid compositions of the present invention generally contain from about 10%, or about 20% up to about 90%, or to about 85% of the fluorine-containing hydrocarbon. In one embodiment, the fluorine-containing hydrocarbon is present in an amount from about 45%, or about 50%, or about 55% up to about 90%, or to about 80%, or to about 75% by weight of the liquid composition. More generally, the liquid compositions will comprise from about 50% to about 99% by weight of the fluorine-containing hydrocarbon. In another embodiment, the liquid compositions contain from about 70% to about 99% by weight of the fluorine-containing hydrocarbon. When the fluorine-containing hydrocarbon is used at levels greater than 50% by weight of the lubricant, then the liquid compositions are generally suited for use as automotive and commercial and industrial refrigeration systems.

In one embodiment, the fluorine-containing hydrocarbon is present in an amount from about 10%, or about 25%, or about 30% up to about 55%, or to about 50%, or to about 45% by weight of the lubricant. When the fluorine-containing hydrocarbon is present in an amount less than about 45%, then the liquid compositions are generally suited for household refrigeration systems.

(B) Carboxylic Ester.

In addition to the fluorine-containing hydrocarbons described above, the liquid compositions also contain a lubricant. The lubricant contains at least one carboxylic ester of a polycarboxylic acylating agent, preferably a dicarboxylic acylating agent and a polyhydroxy compound, or a mixture of monocarboxylic and polycarboxylic acylating agent, preferably dicarboxylic acylating agents and a polyhydroxy compound containing at least two hydroxyl groups and characterized by the general formula



wherein R is a hydrocarbyl group, each R¹ is independently hydrogen, a straight chain lower hydrocarbyl group, a branched chain hydrocarbyl group, or a straight chain hydrocarbyl group containing from about 8 to about 22 carbon atoms provided that at least one R¹ group is hydrogen, a lower straight chain hydrocarbyl or a branched chain hydrocarbyl group, or a carboxylic acid- or carboxylic ester-containing hydrocarbyl group, and n is at

last 2.

The carboxylic ester lubricants utilized as component (B) in the liquid compositions are reaction products of one or more carboxylic acylating agents, e.g. acids or anhydrides (or the lower esters thereof such as methyl, ethyl, etc.), with polyhydroxy compounds containing at least two hydroxyl groups. The polyhydroxy compounds may be represented by the general formula



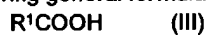
wherein R is a hydrocarbyl group and n is at least 2. The hydrocarbyl group may contain from 4 to about 20 or more carbon atoms, and the hydrocarbyl group may also contain one or more nitrogen and/or oxygen atoms. The polyhydroxy compounds generally will contain from about 2 to about 10 hydroxyl groups and more preferably from about 3 to about 10 hydroxyl groups.

The polyhydroxy compound may contain one or more oxyalkylene groups, and, thus, the polyhydroxy compounds include compounds such as polyetherpolyols. The number of carbon atoms and number of hydroxyl groups contained in the polyhydroxy compound used to form the carboxylic esters may vary over a wide range, and it is only necessary that the carboxylic ester produced with the polyhydroxy compounds be soluble in the liquid compositions.

The polyhydroxy compounds used in the preparation of the carboxylic esters (I) also may contain one or more nitrogen atoms. For example, the polyhydroxy compound may be an alkanolamine containing from 3 to 6 hydroxyl groups. In one preferred embodiment, the polyhydroxy compound is an alkanolamine containing at least two hydroxyl groups and more preferably at least three hydroxyl groups.

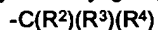
Specific examples of polyhydroxy compounds useful in the present invention include ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, glycerol, neopentyl glycol, 1,2-, 1,3- and 1,4-butanediols, pentaerythritol, dipentaerythritol, tripentaerythritol, triglycerol, trimethylolpropane, di-trimethylolpropane, sorbitol, hexaglycerol, 2,2,4-trimethyl-1,3-pentanediol, etc. Preferably, the mixtures of any of the above polyhydroxy compounds can be utilized.

The carboxylic acylating agents utilized in the preparation of the carboxylic esters useful in the liquid compositions may be characterized by the following general formula



wherein R¹ is (a) H, (b) a straight or branch chain lower hydrocarbyl group (preferably about three to four carbon atoms), (c) a branched chain hydrocarbyl group, or (d) a mixture of one or both of (b) and (c) with a straight chain hydrocarbyl group containing from about 8 to about 22 carbon atoms or (e) a carboxylic acid- or carboxylic acid ester-containing hydrocarbyl group. Stated otherwise, at least one R¹ group in the ester product of Formula I must contain a lower straight chain hydrocarbyl group or a branched chain hydrocarbyl group. The straight chain lower hydrocarbyl group (R¹) contains from 1 to about 7 carbon atoms, and in a preferred embodiment, contains from 1 to about 5 carbon atoms. The branched chain hydrocarbyl group may contain any number of carbon atoms and will generally contain from 4 to about 20 carbon atoms. In one preferred embodiment, the branched chain hydrocarbon group contains from 5 to 20 carbon atoms and in a more preferred embodiment, contains from about 5 to about 14 carbon atoms. The higher molecular weight straight chain hydrocarbyl group containing from 8 to about 22 carbon atoms will contain in some embodiments, from 8 to about 18 carbon atoms, and in more preferred embodiments from 8 to about 14 carbon atoms.

In one embodiment, the branched chain hydrocarbyl groups are characterized by the structure



wherein R², R³ and R⁴ are each independently alkyl groups, and at least one of the alkyl groups contains two or more carbon atoms. Such branched chain alkyl groups, when attached to a carboxyl group are referred to in the industry as neo groups and the acids are referred to a neo acid. The neo acids are characterized as having alpha-alpha-, disubstituted hydrocarbyl groups. In one embodiment, R² and R³ are methyl groups and R⁴ is an alkyl group containing two or more carbon atoms.

Any of the above hydrocarbyl groups (R¹) may contain one or more carboxy groups or carboxy ester groups such as -COOR⁵ wherein R⁵ is a lower alkyl, hydroxyalkyl or a hydroxyalkyloxy group. Such substituted hydrocarbyl groups are present, for example, when the carboxylic acylating agent, R¹COOH (III), is a dicarboxylic acylating agent or a monoester of a dicarboxylic acylating agent. Generally, however, the acid, R¹COOH (III), is a monocarboxylic acid since polycarboxylic acids tend to form polymeric products if the reaction conditions and amounts of reactants are not carefully regulated. Mixtures of monocarboxylic acids and minor amounts of dicarboxylic acids or anhydrides are useful in preparing the esters (I).

Examples of carboxylic acylating agents containing a straight chain lower hydrocarbyl group include formic acid, acetic acid, propionic acid, butyric acid, valeric acid, hexanoic acid and heptanoic acid and anhydrides of any one thereof. Examples of carboxylic acylating agents wherein the hydrocarbyl group is a branched chain hydrocarbyl group include isobutyric acid, 2-ethyl-n-butyric acid, 2-methylbutyric acid, 2,2,4-trimethylpentanoic acid, 2-hexylidcanoic acid, isostearic acid, 2-methylhexanoic acid, 3,5,5-trimethylhexanoic acid, 2-ethyl-

hexanoic acid, isooctanoic acid, isononanoic acid, isohptanoic acid, isodecanoic acid, neohptanoic acid, neodecanoic acid, and ISO Acids and NEO Acids available from Exxon Chemical Company, Houston, Texas USA. ISO Acids are isomeric mixtures of branched acids and include commercial mixtures such as ISO Heptanoic Acid, ISO Octanoic Acid, and ISO Nonanoic Acid, as well as developmental products such as ISO Decanoic Acid, ISO 810 Acid. Of the ISO Acids, ISO Octanoic acid and ISO Nonanoic acid are preferred. Neo acids include commercially available mixtures such as NEO Pentanoic Acid, NEO Heptanoic Acid, and NEO Decanoic Acid, as well as developmental products such as ECR-909 (NEO C₉) Acid, and ECR-903 (NEO C₁₂₁₄) Acid and commercial mixtures of branched chain carboxylic acids such as the mixture identified as NEO 1214 acid from Exxon.

In a preferred embodiment, the ester is prepared from one of the polyhydroxy compound described above and a monocarboxylic acylating agent having from about 4, or about 5, up to about 15, or to about 12, or to about 10 carbon atoms. The monocarboxylic acylating agent may be linear or branched, preferably branched. Particularly useful monocarboxylic acylating agents include branched monocarboxylic acylating agents having 8 or 9 carbon atoms.

The third type of carboxylic acylating agent which can be utilized in the preparation of the carboxylic esters are the acids containing a straight chain hydrocarbyl group containing from 8 to about 22 carbon atoms. As noted previously, these higher molecular weight straight chain acids can be utilized only in combination with one of the other acids described above since the higher molecular weight straight chain acids are not soluble in the fluorohydrocarbons. Examples of such higher molecular weight straight chain acids include decanoic acid, dodecanoic acid, stearic acid, lauric acid, behenic acid, etc.

In another embodiment, the carboxylic acylating agents utilized to prepare the carboxylic esters may comprise a mixture of a major amount of monocarboxylic acylating agents and a minor amount of dicarboxylic acylating agents. Examples of useful dicarboxylic acylating agents include maleic acid or anhydride, succinic acid or anhydride, adipic acid or anhydride, oxalic acid or anhydride, pimelic acid or anhydride, glutaric acid or anhydride, suberic acid or anhydride, azelaic acid or anhydride, sebacic acid or anhydride, etc. The presence of the dicarboxylic acylating agents results in the formation of esters of higher viscosity. The complex esters are formed by having a substantial portion of the dicarboxylic acylating agents react with more than one polyol. The reaction is generally coupling of polyols through the dicarboxylic acylating agent or anhydride. Examples of mixtures of mono- and dicarboxylic acylating agents include succinic anhydride and 3,5,5-trimethylhexanoic acid; azelaic acid and 2,2,4-trimethylpentanoic acid; adipic acid and 3,5,5-trimethylhexanoic acid; sebacic acid and isobutyric acid; adipic and a mixture of 50 parts 3,5,5-trimethylhexanoic acid and 50 parts neoheptanoic acid; and neoheptanoic acid and a mixture of 50 parts adipic acid and 50 parts sebacic acid. The use of mixtures containing larger amounts of dicarboxylic acylating agents should be avoided since the product ester will contain larger amounts of polymeric esters, and such mixtures may be insoluble in the fluorohydrocarbons. An example of such a mixture is 80 parts of neoheptanoic acid and 20 parts of succinic acid. Viscosity and average molecular weight of the ester can be increased by increasing the amount of dicarboxylic acid and decreasing the amount of monocarboxylic acylating agent.

The carboxylic esters of Formula I and the liquid compositions are prepared, as mentioned above, by reacting at least one carboxylic acylating agent with at least one polyhydroxy compound containing at least two hydroxyl groups. The formation of esters by the interaction of carboxylic acylating agents and alcohols is acid catalyzed and is a reversible process which can be made to proceed to completion by use of a large amount of alcohol or carboxylic acylating agent, or by removal of the water as it is formed in the reaction. If the ester is formed by transesterification of a lower molecular weight carboxylic ester, the reaction can be forced to completion by removal of the low molecular weight alcohol formed as a result of a transesterification reaction. The esterification reaction can be catalyzed by either organic acids or inorganic acids. Examples of inorganic acids include sulfuric acids and acidified clays. A variety of organic acids can be utilized including paratoluenesulfonic acid and acidic resins, such as Amberlyst 15, etc. Organometallic catalysts include, for example, tetraisopropoxy orthotitanate.

The amounts of carboxylic acylating agents and polyhydroxy compounds included in the reaction mixture may be varied depending on the results desired. If it is desired to esterify all of the hydroxyl groups containing in the polyhydroxy compounds, sufficient carboxylic acylating agent should be included in the mixture to react with all of the hydroxyl groups. When mixtures of the acylating agents are reacted with a polyhydroxy compound in accordance with the present invention, the carboxylic acylating agents can be reacted sequentially with the polyhydroxy compounds or a mixture of carboxylic acylating agents can be prepared and the mixture reacted with the polyhydroxy compounds. In one embodiment where in mixtures of acylating agents are utilized, the polyhydroxy compound is first reacted with one carboxylic acylating agent, generally, the higher molecular weight branched chain or straight chain carboxylic acylating agent followed by reaction with the straight chain lower hydrocarbyl carboxylic acylating agent.

Throughout the specification and claims, it should be understood that the esters also may be formed by reaction of the polyhydroxy compound with the anhydrides of any of the above-described carboxylic acids. For example, esters are easily prepared by reacting the polyhydroxy compounds either with acetic acid or acetic anhydride.

In one embodiment, the esters are made by reacting a polyol with a mixture of a dicarboxylic acylating agent and a monocarboxylic acylating agent. The amount of dicarboxylic acylating agent and monocarboxylic acylating agent may be varied to obtain a product for the desired result. In one embodiment, one equivalent of polyol is reacted with from about 0.07, preferably from about 0.17 to about 0.33, preferably to about 0.23 moles of dicarboxylic acylating agent and from about 0.67, preferably from about 0.77 to about 0.93, preferably to about 0.83 moles of monocarboxylic acylating agent. Of course, more than one equivalent of acylating agent, and particularly of monocarboxylic acid, may be used.

The formation of esters by the reaction of carboxylic acylating agents with the polyhydroxy compounds described above can be effected by heating the acylating agents, the polyhydroxy compounds, with or without a catalyst to an elevated temperature while removing water, or low molecular weight alcohols or acids formed in the reaction. Generally, temperatures of from about 75°C to about 200°C or higher are sufficient for the reaction. The reaction is completed when water, or low molecular weight alcohol or acid is no longer formed, and such completion is indicated when water, or low molecular weight alcohols or acids can no longer be removed by distillation.

In some instances, it is desired to prepare carboxylic esters wherein not all of the hydroxyl groups have been esterified. Such partial esters can be prepared by the techniques described above and by utilizing amounts of the acid or acids which are insufficient to esterify all of the hydroxyl groups.

The following examples illustrate the preparation of various carboxylic esters (B) which are useful in the liquid compositions of the invention.

Example 1

A mixture of 92.1 parts (1 mole) of glycerol and 316.2 parts of acetic anhydride is prepared and heated to reflux. The reaction is exothermic and continues to reflux at 130°C for about 4.5 hours. Thereafter the reaction mixture is maintained at the reflux temperature by heating for an additional 6 hours. The reaction mixture is stripped by heating while blowing with nitrogen, and filtered with a filter aid. The filtrate is the desired ester.

Example 2

A mixture of 872 parts (6.05 moles) of 2-ethylhexanoic acid, 184 parts (2 moles) of glycerol and 200 parts of toluene is prepared and blown with nitrogen while heating the mixture to about 60°C. Para-toluene sulfonic acid (5 parts) is added to the mixture which is then heated to the reflux temperature. A water/toluene azeotrope distills at about 120°C. A temperature of 125-130°C is maintained for about 8 hours followed by a temperature of 140°C for 2 hours while removing water. The residue is the desired ester.

Example 3

Into a reaction vessel there are charged 600 parts (2.5 moles) of triglycerol and 1428 parts (14 moles) of acetic anhydride. The mixture is heated to reflux in a nitrogen atmosphere and maintained at the reflux temperature (125-130°C) for about 9.5 hours. The reaction mixture is nitrogen stripped at 150°C and 15 mm.Hg. The residue is filtered through a filter aid, and the filtrate is the desired ester.

Example 4

A reaction vessel is charged with 23 parts (0.05 mole) of hexaglycerol and 43.3 parts (0.425 mole) of acetic anhydride. The mixture is heated to the reflux temperature (about 139°C) and maintained at this temperature for a total of about 8 hours. The reaction mixture is stripped with nitrogen and then vacuum stripped to 150°C at 15 mm.Hg. The residue is filtered through a filter aid, and the filtrate is the desired ester.

Example 5

A mixture of 364 parts (2 moles) of sorbitol, and 340 parts (2 moles) of a commercial C₈₁₀ straight chain methyl ester (Procter & Gamble), is prepared and heated to 180°C. The mixture is a two-phase system. Para-toluene sulfonic acid (1 part) is added, and the mixture is heated to 150°C whereupon the reaction commences

and water and methanol evolve. When the solution becomes homogeneous, 250 parts (2.5 moles) of acetic anhydride are added with stirring. The reaction mixture then is stripped at 150°C and filtered. The filtrate is the desired ester of sorbitol.

Example 6

A mixture of 536 parts (4 moles) of trimethylolpropane and 680 parts (4 moles) of a commercial C₈₁₀ straight chain methyl ester is prepared, and 5 parts of tetraisopropoxy orthotitanate are added. The mixture is heated to 200°C with nitrogen blowing. Methanol is distilled from the reaction mixture. When the distillation of methanol is completed by nitrogen blowing, the reaction temperature is lowered to 150°C, and 408 parts (4 moles) of acetic anhydride are added in a slow stream. A water azeotrope begins to evolve when 50 parts of toluene are added. When about 75 parts of a water/acetic acid mixture has been collected, the distillation ceases. Acetic acid (50 parts) is added and additional water/acetic acid mixture is collected. The acetic acid addition is repeated with heating until no water can be removed by distillation. The residue is filtered and the filtrate is the desired ester.

Example 7

A mixture of 402 parts (3 moles) of trimethylolpropane, 660 parts (3 moles) of a commercial straight chain methyl ester comprising a mixture of about 75% C₁₂ methyl ester and about 25% C₁₄ methyl ester, (CE1270 from Procter & Gamble), and tetraisopropoxy orthotitanate is prepared and heated to 200°C with mild nitrogen blowing. The reaction is allowed to proceed overnight at this temperature, and in 16 hours, 110 parts of methanol is collected. The reaction mixture is cooled to 150°C, and 100 parts of acetic acid and 50 parts of toluene are added followed by the addition of an additional 260 parts of acetic acid. The mixture is heated at about 150°C for several hours yielding the desired ester.

Example 8

A mixture of 408 parts (3 moles) of pentaerythritol and 660 parts (3 moles) of the CE1270 methyl ester used in Example 7 is prepared with 5 parts of tetraisopropyl orthotitanate, and the mixture is heated to 220°C under a nitrogen purge. No reaction occurs. The mixture then is cooled to 130°C, and 250 parts of acetic acid are added. A small amount of para-toluenesulfonic acid is added and the mixture is stirred at about 200°C for 2 days, and 60 parts of methanol are removed. At this time, 450 parts of acetic anhydride are added and the mixture is stirred at 150°C until the acetic acid/water azeotrope no longer evolves. The residue is filtered through a filter aid, and the filtrate is the desired ester of pentaerythritol.

Example 9

A mixture of 850 parts (6.25 moles) of pentaerythritol, 3250 parts (25 moles) of neoheptanoic acid, and 10 parts of tetraisopropoxy orthotitanate is prepared and heated to 170°C. Water is evolved and removed by distillation. When the evolution of water ceases, 50 parts of acidified clay are added and some additional water is evolved. A total of about 250 parts of water is removed during the reaction. The reaction mixture is cooled to room temperature and 310 parts of acetic anhydride are added to esterify the remaining hydroxyl groups. The desired ester is obtained.

Example 10

A mixture of 544 parts (4 moles) of pentaerythritol, 820 parts (4 moles) of Neo 1214 acid, a commercial acid mixture available from Exxon, 408 parts (4 moles) of acetic anhydride and 50 parts of Amberlyst 15 is prepared and heated to about 120°C whereupon water and acetic acid begin to distill. After about 150 parts of water/acetic acid are collected, the reaction temperature increases to about 200°C. The mixture is maintained at this temperature of several days and stripped. Acetic anhydride is added to esterify any remaining hydroxyl groups. The product is filtered and the filtrate is the desired ester.

Example 11

A mixture of 1088 parts (8 moles) of pentaerythritol, 1360 parts (8 moles) of a commercial methyl ester of an acid mixture comprising about 55% of C₈, 40% of C₁₀ and 4% of C₆ acids ("CE810 Methyl Ester", Procter

& Gamble), 816 parts of acetic anhydride and 10 parts of paratoluene sulfonic acid is prepared and heated to reflux. About 500 parts of a volatile material are removed. A water azeotrope mixture then distills resulting in the removal of about 90 parts of water. Acetic anhydride (700 parts) is added and the mixture is stirred as a water/acetic acid mixture is removed. The reaction is continued until no more water is evolved and no free hydroxyl groups remain (by IR). The reaction product is stripped and filtered.

Example 12

A mixture of 508 parts (2 moles) of dipentaerythritol, 812 parts (8 moles) of acetic anhydride, 10 parts of acidified clay as catalyst and 100 parts of xylene is prepared and heated to 100°C. This temperature is maintained until the solid dipentaerythritol is dissolved. A water/acetic acid azeotrope is collected, and when the rate of evolution diminishes, the reaction mixture is blown with nitrogen. About 100-200 parts of acetic acid are added and the reaction is continued as additional water/acetic acid/xylene azeotrope is collected. When an infrared analysis of the reaction mixture indicates a minimum of free hydroxyl groups, the reaction mixture is stripped and filtered. The filtrate is the desired product which solidifies.

Example 13

A mixture of 320 parts (1.26 moles) of dipentaerythritol, 975 parts (1.25 moles) of neoheptanoic acid and 25 parts of Amberlyst 15 catalyst is prepared and heated to 130°C. At this temperature water evolution is slow, but when the temperature is raised to 150°C, about 65% of the theory water is collected. The last amounts of water are removed by heating to 200°C. The product is a dark viscous liquid.

Example 14

A mixture of 372 parts (1 mole) of tripentaerythritol, 910 parts (7 moles) of neoheptanoic acid and 30 parts of Amberlyst 15 catalyst is prepared and heated to 110°C as water is removed. The mixture is heated for a total of 48 hours, and unreacted acid is removed by stripping the mixture. The residue is the desired ester.

Example 15

A mixture of 1032 parts (6 moles) of neodecanoic acid, 450 parts (3 moles) of triethylene glycol and 60 parts of Amberlyst 15 is prepared and heated to 130°C. A water azeotrope is evolved and collected. The residue is the desired product.

Example 16

A mixture of 1032 parts (6 moles) of neodecanoic acid and 318 parts (3 moles) of diethylene glycol is prepared and heated to 130°C in the presence of 20 parts of Amberlyst 15. After heating for 24 hours and removing about 90 parts of water, 20 parts of Amberlyst 15 are added and the reaction is conducted for another 24 hours. The reaction is stopped when the theory amount of water is obtained, and the residue is the desired ester.

Example 17

A reaction vessel is charged with 2010 parts (15 moles) of trimethylolpropane, 6534 parts (45 moles) of 2,2,4-trimethylpentanoic acid (available commercially from Exxon Corporation under the trade name ISO Octanoic acid), and 8 parts of methanesulfonic acid. The mixture is heated to 150°C and water is removed. The temperature is increased to 200°C and the temperature is maintained for eight hours. After water evolution, the reaction mixture is vacuum stripped to 200°C and 20 mm Hg. The residue is filtered and the filtrate is the desired product. The product has a neutralization acid number of 0.06 and a kinematic viscosity of 32 cSt at 40°C.

Example 18

A reaction vessel is charged with 2814 parts (21 moles) of trimethylolpropane, 6854 parts (67 moles) of isopentanoic acid (available commercially from Union Carbide), which is a mixture of 66% by weight valeric acid and 34% by weight 2-methylbutyric acid, 5 parts of methanesulfonic acid, 50 parts of an aromatic solvent. The reaction mixture is heated to 145°C over three hours. The reaction mixture is heated to 165°C over three

hours. The temperature of the mixture is maintained for 13 hours. A total of 1100 milliliters of water is collected. The reaction mixture is vacuum stripped to 180-200°C and 10-15 mm Hg. The residue is filtered and the filtrate is the desired product. The product has a 0.009 acid number, and a kinematic viscosity of 10.2 cSt at 40°C and 2.65 cSt at 100°C.

Example 19

A reaction vessel is charged with 2345 parts (17.5 moles) of trimethylolpropane, and 8295 parts (52.5 moles) of 3,5,5 trimethylhexanoic acid (available commercially from Exxon Corporation under the trade name ISO Nonanoic acid). The mixture is heated to 150°C and the temperature is maintained for 12 hours. The reaction mixture is then heated to 200°C and the temperature is maintained for 38 hours. The reaction is then heated to 220°C and the temperature is maintained for 14 hours. The reaction mixture is vacuum stripped to 200°C and 10-15 mm Hg. Alumina (275 parts) is added to the residue and the residue is filtered. The filtrate is the desired product. The product has a zero acid number, and a kinematic viscosity of 52.8 cSt at 40°C and 7.1 cSt at 100°C.

Example 20

A mixture of 200 parts (2 moles) of succinic anhydride and 62 parts (1 mole) of ethylene glycol is heated to 120°C, and the mixture becomes a liquid. Five parts of acidic clay are added as catalyst, and an exotherm to about 180°C occurs. Isooctanol (260 parts, 2 moles) is added, and the reaction mixture is maintained at 130°C as water is removed. When the reaction mixture becomes cloudy, a small amount of propanol is added and the mixture is stirred at 100°C overnight. The reaction mixture then is filtered to remove traces of oligomers, and the filtrate is the desired ester.

Example 21

A mixture of 200 parts (2 moles) of succinic anhydride, 62 parts (1 mole) of ethylene glycol and 1 part of paratoluene sulfonic acid is prepared and heated to 80-90°C. At this temperature, the reaction begins and an exotherm to 140°C results. The mixture is stirred at 130-140°C for 15 minutes after 160 parts (2 moles) of 2,2,4-trimethylpentanol are added. Water evolves quickly, and when all of the water is removed, the residue is recovered as the desired product.

Example 22

A mixture of 294 parts (3 moles) of maleic anhydride and 91 parts (1.5 moles) of ethylene glycol is prepared and heated at about 180°C whereupon a strong exotherm occurs and the temperature of the mixture is raised to about 120°C. When the temperature of the mixture cools to about 100°C, 222 parts (3 moles) of n-butyl alcohol and 10 parts of Amberlyst 15 are added. Water begins to evolve and is collected. The reaction mixture is maintained at 120°C until 50 parts of water is collected. The residue is filtered, and the filtrate is the desired product.

Example 23

A mixture of 1072 parts (8 moles) of trimethylolpropane, 2080 parts (16 moles) of neoheptanoic acid and 50 parts of Amberlyst 15 is prepared and heated to about 130°C. A water/acid azeotrope evolves and is removed. When about 250 of the azeotrope has been removed, 584 parts (4 moles) of adipic acid are added and the reaction continues to produce an additional 450 parts of distillate. At this time, 65 parts of trimethylolpropane are added to the mixture and additional water is removed. The residue is filtered and the filtrate is the desired ester.

Example 25

Esters are prepared by reacting mixtures of isononanoic acid (1) and adipic acid (2) with trimethylolpropane (3), in the presence of a tetraisopropoxy orthotitanate catalyst. The reactants are charged to a flask and heated until reaction ceases, as indicated by termination of water collection in a distillation trap, at which point the reaction mixture has reached about 220°C. A vacuum is applied to remove volatile components, and the flask contents are cooled and filtered to produce the liquid ester product.

Properties of the products are as follows:

	Moles			Catalyst,	Viscosity, cSt		Molecular
Product	(1)	(2)	(3)	grams	40°C	100°C	Weight
A	44	2	16	13	76.6	9.1	611
B	40	4	16	12	116	12.3	694
C	16	2	6.7	5	141	13.9	723

As can be seen, increasing the fraction of dicarboxylic acid results in a higher viscosity, higher average molecular weight (as measured by vapor phase osmometry) ester material.

Example 26

The procedure of Example 25 is used to prepare esters from isononanoic acid (1), adipic acid (2) and neopentylglycol (3), giving the following product properties:

	Moles			Catalyst,	Viscosity, cSt		Molecular
Product	(1)	(2)	(3)	grams	40°C	100°C	Weight
A	2	1	2	2	80	10.5	588
B	10.7	6.7	12	5	106	13.2	665
C	8.3	8.3	12.5	8	220	22.1	758

Example 27

The procedure of Example 25 is used to prepare esters from isononanoic acid (1), isooctanoic acid (2), isobutyric acid (3), adipic acid (4) and pentaerythritol (5), giving the following product properties:

	Moles					Catalyst
Product	(1)	(2)	(3)	(4)	(5)	grams
A	7	7	7	1.5	6	5
B	7.2	7.2	6	1.8	6	5

Product	Viscosity, cSt		Molecular
	40°C	100°C	Weight
A	149.5	14.0	733
B	194	16.9	802

Example 28

The procedure of Example 25 is used to prepare the ester in Table 3.

TABLE 3

Example	Moles		
	TMP(1)	Adipic	iso Nonanoic
		Acid	Acid (2)
Comparative Example	1	0	3
28A	1	0.1	2.8
28B	1	0.125	2.75
28C	1	0.25	2.45
28D	1	0.30	2.4
28E	1	0.35	2.3

Example	Viscosity	
	@40°C	@100°C
Example	52.25	7.25
28A	69.4	8.65
28B	76.6	9.14
28C	119	12.3
28D	140	14
28E	185	16.8

(1) TMP - Trimethylolpropane

(2) Available from Exxon Chemical Company

As can be seen from Table 3, as the level of dicarboxylic acid is increased, the viscosity of the ester increases.

The carboxylic ester lubricants preferably contain branched alkyl groups and generally are free of acetylenic and aromatic unsaturation. Some ester which contain such unsaturation may be insoluble in the fluorine-containing hydrocarbons. In one embodiment, the soluble ester lubricants of this invention also are preferably free of olefinic unsaturation except that some olefinic unsaturation may be present so long as the lubricant is soluble.

The carboxylic esters are soluble in the fluorine-containing hydrocarbons and, in particular, in the fluorohydrocarbons such as 1,1,1,2-tetrafluoroethane. The carboxylic esters are soluble over a wide temperature range and, in particular, at low temperatures. The solubility of the lubricants in fluorohydrocarbons such as 1,1,1,2-tetrafluoroethane at low temperatures is determined in the following manner. The lubricant (0.5 gram) is placed in a thick-walled glass vessel equipped with a removable pressure gauge. The tetrafluoroethane (4.5 grams) is condensed into the cooled (-40°C) glass vessel, and the contents are warmed to the desired temperature and mixed to determine if the lubricant is soluble in the tetrafluoroethane. If soluble, the temperature of the mixture is reduced until a separation and/or precipitate is observed. The results of this solubility test conducted with several examples of the carboxylic ester lubricants are summarized in the following Table II.

TABLE II

Liquid Containing Product of Examl	Solubility °C (ppt.)
6	-45
10	-50
11	-40
12	-50
13	-15
15	-30
16	10
17	-29
19	-40
20	-25
22	-10
25(A)	-35
25(B)	-30
25(C)	-30

In one embodiment, the liquid compositions comprise a major amount of a fluorine-containing hydrocarbon and a minor amount of at least one soluble organic lubricant comprising at least one carboxylic ester. By "major amount" is meant an amount greater than 50% by weight such as 50.5%, 70%, 99%, etc. The term "minor amount" includes amounts less than 50% by weight such as 1%, 5%, 20%, 30% and up to 49.9%. In one embodiment, the liquid compositions will comprise from about 70% to about 99% of the fluorine-containing hydrocarbon and from about 1 to about 30% by weight of the lubricant. In other embodiment, the liquid compositions may contain from about 5% to about 20% by weight of the lubricant.

The liquid compositions may additionally contain (C) at least one additive selected from the group consisting of an alkyl phosphite, an alkyl phosphonic acid ester, a nitrogen-containing heterocycle, and a mixture thereof. The phosphite and/or the alkyl phosphonic acid ester are present in an amount sufficient to provide antiwear and/or extreme pressure properties to the lubricant and liquid composition. The phosphite and/or the alkyl phosphonic acid ester are present in an amount to provide 0.001%, or to 0.015%, or about 0.025%, to about 1%, or to about 0.5%, or to about 0.2% by weight phosphorus to the lubricant. The nitrogen-containing heterocycle is present in an amount from about 0.001%, or about 0.02%, or about 0.03% up to about 5%, or to about 2%, or to about 1%, or to about 0.5% by weight of the lubricant.

The phosphite and/or the alkyl phosphonic acid ester provide beneficial antiwear and extreme pressure properties to the liquid compositions. The phosphite may be a dialkyl or trialkyl phosphite, preferably a dialkyl phosphite. The alkyl phosphonic acid ester may be an alkyl phosphonic acid diester, preferably a dialkylester. The alkyl groups of the phosphite and the phosphonic acid ester independently contain from 1, or about 3 to about 20, or to about 18, or to about 8 carbon atoms. In one embodiment, the phosphite and the phosphonic acid ester have alkyl groups independently containing from about 3 to about 6, or to about 5 carbon atoms. A number of dialkyl phosphites are commercially available, such as lower dialkyl phosphites, which are preferred. Lower dialkyl phosphites include dimethyl, diethyl, dipropyl, dibutyl, dipentyl and dihexyl phosphites. Phosphites and their preparation are known and many phosphites are available commercially. Also mixed alkyl phosphites, made from a mixture of alcohols, are useful in the present invention. Examples of mixtures of alcohols include thyl and butyl alcohol; propyl and pentyl alcohol; and methyl and pentyl alcohol. A particularly useful phosphite is dibutyl phosphite.

Alkyl phosphonic acid esters are prepared by means known to those in the art. For example, alkyl phosphonic acid esters may be prepared by reacting an alkyl halide with a trialkyl phosphite. Examples of alkyl phosphonic acid esters include diethyl, butylphosphonate; dibutyl, butylphosphonate; 2-ethylhexyl, 2-ethylhexylphosphonate, etc.

The lubricant may additionally contain a nitrogen-containing heterocycle, such as dimercaptotriadiazoles,

triazoles, amino-mercaptotriadiazoles, imidazoles, thiazoles, tetrazoles, hydroxyquinolines, oxazolines, imidazolines, thiophenes, indoles, indazoles, quinolines, benzoxazines, dithiols, oxazolones, s-triazoles, pyridines, piperazines, triazines, and derivatives of any one or more thereof. In one embodiment, the nitrogen containing heterocycle is a triazole or derivative thereof, a thiazole or derivative thereof, a mercaptotriazole or derivative thereof and a thiadiazole or derivative thereof, preferably a triazole or derivative thereof. These additives provide metal deactivating, metal passivating and corrosion controlling character to the liquid compositions. Examples of useful metal deactivators include dimercaptotriadiazoles and derivatives thereof, substituted and unsubstituted triazoles (e.g., benzotriazole, tolyltriazole, octylbenzotriazole, and the like), mercaptobenzothiazoles, etc. Examples of these compounds are benzotriazole, alkyl-substituted benzotriazole (e.g., tolyltriazole, ethylbenzotriazole, hexylbenzotriazole, octylbenzotriazole, etc.), aryl-substituted benzotriazole (e.g., phenol benzotriazoles, etc.), and alkylaryl- or arylalkyl-substituted benzotriazole and substituted benzotriazoles where the substituent may be hydroxy, alkoxy, halo (especially chloro), nitro, carboxy and carboxyalkoxy. Preferably, the triazole is a benzotriazole or an alkylbenzotriazole in which the alkyl group contains 1 to about 20 carbon atoms, preferably 1 to about 8 carbon atoms.

The nitrogen containing heterocycle (C) may also be the reaction product of at least one of the above triazoles, at least one amine and an aldehyde or aldehyde precursor. The triazole is preferably a benzotriazole. The amine can be one or more mono- or polyamines. These monoamines and polyamines can be primary amines, secondary amines or tertiary amines. Examples of polyamines include polyalkylenepolyamines, and heterocyclic polyamines. The polyalkyleneamines include polyethylenepolyamines, such as diethylenetriamine, triethylenetrimine, tetraethylenepentaamine, etc.

The aldehyde is typically a hydrocarbon-based aldehyde, preferably a lower aliphatic aldehyde. Suitable aldehydes include formaldehyde, benzaldehyde, acetaldehyde, the butyraldehydes, hydroxybutyraldehydes and heptanals, as well as aldehyde precursors which react as aldehydes under the conditions of the reaction such as paraformaldehyde, paraldehyde, formalin and methanal. Formaldehyde and its precursors (e.g., paraformaldehyde, trioxane) are preferred. Mixtures of aldehydes may be used.

An example of a useful triazole derivative is Reomet® 39. This material is a triazole derivative available commercially from Ciba-Geigy Corporation.

The liquid compositions are characterized as having improved thermal and chemical stability over a wide temperature range. The liquid compositions have improved antiwear and corrosion stability properties. The liquid compositions have beneficial viscosity properties. Preferably the liquid compositions have a viscosity of 5-400 centistokes (cSt) measured at 40°C.

Liquid compositions containing carboxylic esters derived from neo polyols such as neopentylglycol, trimethylolpropane and pentaerythritol, have beneficial thermal and hydrolytic stability. Liquid compositions containing carboxylic esters derived from branched acids, such as iso or neo acids, preferably neo acids, have improved thermal and hydrolytic stability. In one embodiment, the carboxylic esters are derived from the above polyols, a polycarboxylic acid and an iso or neo acid. The liquid composition may contain one carboxylic ester reaction product or in another embodiment, the liquid compositions may contain a blend of two or more carboxylic ester reaction products. A liquid composition of a desired viscosity may be prepared by blending a higher viscosity carboxylic ester with a lower viscosity carboxylic ester. Other additives, if soluble in the liquid, known to be useful for improving the properties of halogen-containing hydrocarbon refrigerants can be included in the liquid compositions to improve the characteristics of the liquid as a refrigerant. However, hydrocarbon oils such as mineral oil generally are not included in and are most often excluded from the liquid compositions of the invention, particularly when the fluorine-containing hydrocarbon contains no other halogens. Hydrocarbon lubricants, however, may be present if the liquid compositions are used to retrofit a compressor system which had previously used a hydrocarbon lubricant.

Other additives may be included in the liquid compositions of the present invention to enhance the performance of the liquids include extreme-pressure and anti-wear agents, oxidation and thermal-stability improvers, corrosion-inhibitors, viscosity-index improvers, pour point and/or floc point depressants, detergents, dispersants, anti-foaming agents, viscosity adjusters, metal deactivators, etc. As noted above, these supplementary additives must be soluble in the liquid compositions of the invention. Included among the materials which may be used as extreme-pressure and antiwear agents are phosphates, phosphate esters, thiophosphates such as zinc diorganodithiophosphates, chlorinated waxes, sulfurized fats and olefins, organic lead compounds, fatty acids, molybdenum complexes, borates, halogen-substituted phosphorous compounds, sulfurized Diels Alder adducts, organic sulfides, metal salts of organic acids, etc. Sterically hindered phenols, aromatic amines, dithiophosphates, sulfides and metal salts of dithioacids are useful examples of oxidation and thermal stability improvers. Compounds useful as corrosion-inhibitors include organic acids, organic amines, organic phosphates, organic alcohols, metal sulfonates, etc. VI improvers include polyol fins such as polyether, polybutene, polymethacrylates, polyalkylstyrenes, etc. Pour point and floc point depressants include polymers

thacrylates, thyl n - vinyl acetate copolymers, succinamic acid-olefin copolymers, thyl ne-alpha olefin co-
 polymers, tc. D t rg nts include sulfonates, long-chain alkyl-substituted aromatic sulfonic acids, phenylates,
 metal salts of alkyl phenols, alkyl ph nol-aldehyde condensation products, metal salts of substitut d salicylates,
 5 etc. Silicone polymers are a well known type of anti-foam agent. Viscosity adjusters are exemplified by poly-
 sobutylene, polymethacrylates, polyalkyl styrenes, naphthenic oils, alkyl benzene oils, polyesters, polyvinyl
 chloride, polyphosphates, etc.

The following examples (TABLE 1) relate to formulations which are useful as organic lubricant (B) in the
 present invention.

10

15

20

25

30

35

40

45

50

55

TABLE I

Product of Ex.	I	II	III	IV	V	VI	VII	VIII	IX	X
2	99.38	99.5	99.18	99.1	99.8	99.88	99.85			99.5
25C								99.9		
25B									99.4	
DBPH ¹	0.62	0.5		0.6	0.1	0.1	0.1		0.5	0.1
DBBP ²			0.62							0.1
Tolyltriazole						0.02	0.05	0.1		
Oleyamide			0.2		0.1				0.1	0.1
Reomet® 39 ³				0.3						0.2

(1) Dibutyl phosphite, (2) Dibutylbutylphosphonate,

(3) Reomet® 39 is a triazole derivative available commercially from Ciba-Geigy Corp.

The liquid compositions of the present invention are particularly useful as refrigerants in various refrigeration systems which are compression-type systems such as refrigerators, freezers, and air-conditioners including automotive, home and industrial air-conditioners. The following examples are illustrative of the liquid compositions of the present invention.

	Parts by Wt.
<u>Example A</u>	
1,1,1,2-tetrafluoroethane (HFC-134a)	90
Lubricant of Example 17	10
DBPH	0.625
Benzotriazole	0.02
<u>Example B</u>	
1,1,1,2-tetrafluoroethane	85
Lubricant of Example 19	15
DBBP	0.2
<u>Example C</u>	
HFC-134a	55
Lubricant of Example 6	45
Dibutyl phosphite	0.05
benzotriazole	0.01
<u>Example D</u>	
HFC-134a	60
Product of Example 18	40
tolyltriazole	0.025
<u>Example E</u>	
HFC-134a	85
Product of Example 19	15
Reomet® 39	0.02

Table 2 contains further examples of the liquid compositions of the present invention.

Table 2

	F	E	H	I	J
HFC-134	80	85	55	90	45
Lubricant of Example:					
I	20				
V		15		10	
VII			45		55

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

Cross-Reference to Related Applications

This application is related to U.S. Serial No. 07/728,441 filed July 11, 1991, which is a continuation-in-part of U.S. Serial No. 608,600 filed on October 30, 1990, which is a continuation of Serial No. 343,087 filed on April 25, 1989 and now abandoned, the disclosures of which are hereby incorporated in their entirety.

Example References	
Example	Source
1-16	2456-02
17	1069N-133
18	928N-3
19	1066n-59
20-28	2456-02

Claims

1. A liquid composition comprising:
 - (A) at least one fluorine-containing hydrocarbon containing 1 to 3 carbon atoms, and a lubricant comprising
 - (B) at least one ester lubricant selected from (i) an ester of a polyhydroxy compound and a monocarboxylic acylating agent having from about 4 to about 15 carbon atoms or mixtures thereof, and (ii) an ester of polyhydroxy compound and a combination of a dicarboxylic acylating agent and a monocarboxylic acylating agent having about 4 to about 15 carbon atoms, and
 - (C) at least one additive selected from an alkyl phosphite, an alkyl phosphonic acid ester, a nitrogen-containing heterocycle, and a mixture thereof.
2. A liquid composition consisting essentially of (A) at least one fluorine-containing hydrocarbon containing 1 to 3 carbon atoms, and a lubricant comprising (B) at least one soluble ester lubricant selected from (i) an ester of polyhydroxy compound and a monocarboxylic acylating agent having from about 4 to about 15 carbon atoms, or a mixture thereof, and (ii) an ester of polyhydroxy compound and a combination of a dicarboxylic acylating agent and a monocarboxylic acylating agent having about 4 to about 15 carbon atoms, and (C) at least one additive selected from an alkyl phosphite, an alkyl phosphonic acid ester having independently from about 1 to about 20 carbon atoms in each alkyl group, a nitrogen containing heterocycle or derivative thereof, and a mixture thereof.
3. The liquid composition of either of claims 1 and 2 wherein fluorine is the only halogen in the fluorine-containing hydrocarbon (A).
4. The liquid composition of any preceding claim wherein the fluorine-containing hydrocarbon (A) is 1,1,1,2-tetrafluoroethane.
5. The liquid composition of any preceding claim wherein the ester (B) is (i) and the polyhydroxy compound is selected from neopentyl glycol, glycerol, trimethylolpropane, di-trimethylolpropane, pentaerythritol, dipentaerythritol, and tripentaerythritol.
6. The liquid composition of any preceding claim wherein the polyhydroxy compound is trimethylolpropane.
7. The liquid composition of any preceding claim wherein the monocarboxylic acylating agent is a branched monocarboxylic acylating agent having 8 or 9 carbon atoms.
8. The liquid composition of any preceding claim wherein the monocarboxylic acylating agent is a mixture of (a) a monocarboxylic acylating agent having four or five carbon atoms and (b) a monocarboxylic acylating agent having about 7 to about 15 carbon atoms.

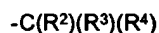
9. The liquid composition of any preceding claim wherein (a) is isobutyric, valeric, 2-methylbutyric, or neopentanoic acid or anhydride, and (b) is a branched monocarboxylic acylating agent having 8 or 9 carbon atoms.
10. The liquid composition of any preceding claim wherein the ester (B) is (ii) and the polyhydroxy compound is selected from trimethylolpropane, pentaerythritol, dipentaerythritol, and tripentaerythritol.
11. The liquid composition of claim 10 wherein the polyhydroxy compound is trimethylolpropane.
12. The liquid composition of any preceding claim the monocarboxylic acylating agent is a branched monocarboxylic acylating agent having 8 or 9 carbon atoms, and the dicarboxylic acylating agent contains from about 2 to about 12 carbon atoms.
13. The liquid composition of any preceding claim wherein the dicarboxylic acylating agent is adipic acid.
14. The liquid composition of any preceding claim wherein (C) is an alkyl phosphite or an alkyl phosphonic acid ester which contains independently about 1 to about 20 carbon atoms in each alkyl group.
15. The liquid composition of any preceding claim wherein (C) is an alkyl phosphite or an alkyl phosphonic acid ester independently having from about 3 to about 8 carbon atoms in each alkyl group.
16. The liquid composition of any preceding claim wherein (C) is dibutyl phosphite.
17. The liquid composition of any preceding claim wherein (C) is dibutyl, butyl phosphonate.
18. The liquid composition of any preceding claim wherein (C) is a triazole or derivative thereof.
19. The liquid composition of any preceding claim wherein (C) is tolytriazole, benzotriazole, or a reaction product of a benzotriazole, an amine, and an aldehyde or aldehyde precursor.
20. The liquid composition of any preceding claim wherein (C) is a mixture of an alkyl phosphite independently having from about 1 to about 20 carbon atoms in each alkyl group, and a triazole or derivative thereof.
21. A liquid composition comprising: (A) at least one fluorine-containing hydrocarbon containing 1 to 2 carbon atoms, and a lubricant comprising (B) at least one ester selected from (i) an ester of a polyhydroxy compound and a monocarboxylic acylating agent selected from branched monocarboxylic acylating agents having from about 4 to about 20 carbon atoms, straight chain monocarboxylic acylating agents having from 8 to about 22 carbon atoms, and mixtures thereof, and (ii) an ester of a polyhydroxy compound and a combination of a dicarboxylic acylating agent and a monocarboxylic acylating agent selected from branched monocarboxylic acylating agents having from about 4 to about 20 carbon atoms, straight chain monocarboxylic acylating agents having from 8 to about 22 carbon atoms, and mixtures thereof, and (C) at least one additive selected from an alkyl phosphite, an alkyl phosphonic acid ester, a nitrogen containing heterocycle, and a mixture thereof.
22. A liquid composition comprising:
 - (A) a major amount of at least one fluorine-containing hydrocarbon containing 1 or 2 carbon atoms;
 - (B) a minor amount of at least one soluble organic lubricant comprising at least one carboxylic ester of a polyhydroxy compound containing at least 2 hydroxyl groups and characterised by the general formula

$$R[OC(O)R^1]_n \quad (I)$$
 wherein R is a hydrocarbyl group, each R¹ is independently hydrogen, a straight chain lower hydrocarbyl group, a branched chain hydrocarbyl group, or a straight chain hydrocarbyl group containing from 8 to about 22 carbon atoms provided that at least one R¹ group is hydrogen, a lower straight chain hydrocarbyl or a branched chain hydrocarbyl group, or a carboxylic acid- or carboxylic acid ester-containing hydrocarbyl group, and n is at least 2; and (C) a phosphite.
23. The liquid composition of claim 22 wherein R¹ in Formula I is a branched chain hydrocarbyl group containing from about 4 to about 20 carbon atoms.
24. The liquid composition of either of claims 22 and 23 wherein n in Formula I is an integer from 2 to about 10.

25. The liquid composition of any one of claims 22 to 24 wherein (B) is a carboxylic ester of trimethylolpropan , pentaerythritol, dipentaerythritol or tripentaerythritol.

26. The liquid composition of any one of claims 22 to 25 wherein at least one of the R¹ groups is hydrogen or a methyl or ethyl group and the remaining R¹ groups are branched chain alkyl groups containing from 5 to about 20 carbon atoms.

27. The liquid composition of any one of claims 22 to 26 wherein the branched chain alkyl groups are characterised by the structure



wherein R², R³ and R⁴ are each independently alkyl groups and at least one of the alkyl groups contain 2 or more carbon atoms.

28. The liquid composition of any one of claims 22 to 27 wherein (C) is an alkyl phosphite independently having from 1 to about 20 carbon atoms in each alkyl group.

29. The liquid composition of any one of claims 22 to 28 wherein (C) is dibutyl phosphite.

30. A liquid composition comprising: (A) at least one fluorine-containing hydrocarbon containing 1 or 2 carbon atoms; and a lubricant comprising (B) at least one soluble organic lubricant comprising at least one carboxylic ester of a polyhydroxy compound containing at least 2 hydroxyl groups and characterised by the general formula



wherein R is a hydrocarbyl group, each R¹ is independently hydrogen, a straight chain lower hydrocarbyl group, a branched chain hydrocarbyl group, or a straight chain hydrocarbyl group containing from 8 to about 22 carbon atoms provided that at least one R¹ group is hydrogen, a lower straight chain hydrocarbyl or a branched chain hydrocarbyl group, or a carboxylic acid- or carboxylic acid ester-containing hydrocarbyl group, and n is at least 2; and (C) an additive selected from an alkyl phosphite, an alkyl phosphonic acid ester, a nitrogen-containing heterocycle, and a mixture thereof.

31. A method of lubricating a refrigeration system comprising the steps of introducing into the refrigeration system a composition according to any preceding claim; and operating the system.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 30 3329
Page 1

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 470 788 (NIPPON OIL CO.) * page 3, line 50 - page 4, line 20 * * page 4, line 58 - page 5, line 5 * * page 6, line 11 * * page 7, line 2 * ---	1-7, 14-16, 18,19, 21-31	C10M105/38 C10M105/42 C10M169/04 C10M171/00 //(C10M169/04, 105:38,105:42, 133:44,137:02, 137:12) (C10N40:30)
X	EP-A-0 475 751 (KAO CORPORATION) * page 3, line 29 - line 36 * * page 7, line 19 - line 22 * * page 10; table 1 * ---	1-7,18, 19, 21-25, 30,31	
X	EP-A-0 448 402 (ASAHI DENKA KOGYO KABUSHIKI KAISHA) * page 4, line 2 * * page 4; examples 3,4 * * page 5; example 15 * ---	1-6,8, 10,11, 13,14,31	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
P,X	EP-A-0 501 440 (KAO CORPORATION) * page 6, line 58 - page 7, line 7 * * page 9; example c; table 1 * --- -/--	1-7, 10-13, 18,19, 21,31	C10M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 09 JULY 1993	Examiner HILGENGA K.J.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 OL82 (P06001)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 30 3329
Page 2

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 435 253 (NIPPON OIL COMPANY) * page 7, line 37 * * page 8, line 17 * * page 8; example 1 * * page 9; example 8 * * page 12; examples 22,23 * ---	1-7,10, 11, 13-16, 18,19, 21,31	
X	WO-A-9 118 073 (THE LUBRIZOL CORPORATION) * page 11, line 4 - line 18 * * page 15, line 1 - line 12 * * page 20, line 6 - line 16 * * page 29, line 9 - line 22 * * page 31, line 30 - page 32, line 8 * * page 35; example 17 * * page 39; example 28 * * page 42; example D * ---	1-7,10, 11, 13-15, 21-27, 30,31	
A		17	
P,X	EP-A-0 510 633 (JAPAN SUN OIL) * page 10, line 39 - line 41 * * page 11, line 14 * * page 14; example 3 * * page 17; example 32 * ---	1-5,14, 15,18, 19,21,31	
X	EP-A-0 415 778 (KAO CORPORATION) * page 5, line 41 * * page 7; table 1 * * claim 1 * ---	1-7, 10-14, 21,31	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
Place of search THE HAGUE		Date of completion of the search 09 JULY 1993	Examiner HILGENGA K.J.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document</p>			

EPO FORM 1503 (03/92) (P0401)



**European Patent
Office**

EUROPEAN SEARCH REPORT

Application Number

EP 93 30 3329

Page 3

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	US-A-5 021 179 (E.R ZEHLER) * column 6, line 6 * * column 6, line 53 * * column 7, line 40 - line 48; table 2 * -----	1-9,14, 18,19, 21-25, 30,31	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
The present search report has been drawn up for all claims			
Place of search THE HAGUE	Date of completion of the search 09 JULY 1993	Examiner HILGENGA K.J.	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			